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Green Chemistry for Stainless Steel Corrosion Resistance: Life Cycle Assessment (LCA) of Citric Acid versus Nitric Acid Passivation

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Abstract

Corrosion is a significant problem in many industries, and when using stainless steel, passivation is undertaken to improve corrosion resistance.

Traditionally, nitric acid is used within the passivation step, however, this has some detrimental environmental and human health impacts during its production and use. Reducing this impact is critical, and because of its toxicity, associated occupational risk and special disposal requirements, end-users of passivated stainless steels are exploring alternative passivation methods. However, it is also critical to understand the impact of any alternatives. Sustainable processing and manufacture embodies many elements, including; waste reduction, resource efficiency measures, energy reduction and the application of 'green' or renewable chemicals. In order to ensure the most effective system is utilised the impact, or potential impact of the system must be measured and options compared. The comparative environmental credentials of bio-based chemicals can be assessed using tools such as Life Cycle Assessment (LCA).

This paper is the first paper to evaluate the environmental impact of passivation using nitric and citric acid. It uses attributional Life Cycle Assessment (ALCA) to assess the environmental benefits and dis-benefits of using citric acid - produced biologically via fermentation, to replace nitric acid, whilst keeping the same level of corrosion resistance. The work is anticipatory in nature as the process is not yet undertaken on a commercial basis. The results therefore feed into future manufacturing and design.

Citric and nitric acids were compared using three different solutions: 4% and 10% citric acid solutions, and a 10% nitric acid solution (the conventional case). The results show that a scenario using a 4% citric acid solution is environmentally preferable to nitric acid across all impact categories assessed. However, a 10% citric acid solution used on low chromium and nickel steel was only environmentally preferable for 50% of the environmental impact categories assessed due to increased electrical energy demand for that scenario.

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Highlights

- Citric acid is environmentally preferable to nitric acid for stainless steel passivation
- Extent is dependent on passivation bath conditions for comparable performance
- Life cycle approach is key to understanding nuances of environmental impact for stainless steel passivation

Key words

Stainless steel, passivation, environmental impact, life cycle assessment, LCA

1.0 Introduction

Sustainability has become an increasingly important element in materials manufacture, leading to focus on process energy reduction and the application of green chemistry and other eco-design principles. The term 'green chemistry' gained traction during the 1990's culminating in formal recognition through the publication of the 12 principles of green

48   chemistry [1]. The guiding element to this being 'benign by design'. The principles provide a

49   toolkit for employing ideas embedded in industrial ecology [2]. The Environmental Protection

50   Agency (EPA) definition of green chemistry is 'the design of chemical products and

51   processes that reduce or eliminate the use or generation of hazardous substances. Green

52   chemistry applies across the life cycle of a chemical product, including its design,

53   manufacture, use, and ultimate disposal' [3].

54   Metrics for green chemistry include the *Efactor* defined as the amount of waste produced per

55   kilogram (product) [4], *reaction mass efficiency* or *carbon efficiency* [5]], and *Cfactor* which is

56   the mass ratio of CO_2 to product mass [6], however, it does not distinguish between fossil

57   and biogenic CO_2 emissions.

58   Given that the overarching aim of green chemistry employs life cycle thinking and a

59   consideration for the whole chemical product system, techniques like Life Cycle Assessment

60   (LCA) are often used to quantitatively assess the potential environmental impacts of bio-

61   based/renewable solvents or resource efficiency measures [7, 8]. LCA evaluates

62   environmental impact of a chemical process from raw materials production all the way

63   through to end-of-life [9]. It is a comparative assessment method, meaning that is can be

64   usefully applied to compare 'green' and conventional production methods. Unlike the green

65   chemistry metrics, LCA also enables the comparison of production processes across a

66   number of different environmental impact categories. ISO standards 14040 and 14044 set

67   out procedures and methodologies for carrying out an LCA study [10, 11]. LCA has four

68   main components: goal and scope definition, life cycle inventory (LCI), life cycle impact

69   assessment (LCIA), and interpretation [10]. The goal and scope definition describes the

70   product or process under assessment and details the purpose of the study. In the life cycle

71   inventory step data is collected to then be analysed in the impact assessment stage.

72   There are a number of challenges in applying LCA to green chemistry and biotechnology. At

73   design or process development stages, LCA is often seen as too complex when evaluating

74   different materials, processing or solvent options – particularly where there is high

75   uncertainty on what the process may look like at scale. Another challenge is the availability

76   of industrial production data for many biologically derived chemicals and solvents. In order to

77   overcome some of these issues, key parameters for LCA of green chemicals have

78   previously been identified in [12]. Never the less, LCA still remains an important assessment

79   tool in determining comparative impact for bio-based chemicals across a range of

80   environmental impact criteria.

81   Passivation of stainless steel is an important process to improve corrosion resistance. For

82   example, within the space industry stainless steels are used in spacecraft and ground

83   support structures where corrosion risk is high, including the storage and handling of certain

84   liquids and wastes, propulsion systems, and components and fasteners exposed to harsh or

85   demanding environments [13]. The effects of corrosion can have substantial economic and

86   safety impacts, and lead to prolonged periods of asset downtime. The passivation process

87   removes anodic surface contaminants (e.g. iron compounds) via chemical dissolution and

88   leads to the formation of a passive oxide layer. The most commonly used acid to do this is

89   nitric acid. Nitric acid is produced via ammonia oxidation. The process emits nitrous oxides

90   (NO_x) and ammonia (NH_3) [14]. Nitric acid is highly corrosive and toxic on inhalation, and

91   whilst it does feature on the EPA's safer chemical choice list for its application as a

92   processing aid and additive, it is recognised as having some hazard profile issues and is not

93   necessarily a low level of hazard concern for all human health and environmental endpoints

94   [15]. Because of its toxicity, associated occupational risk and special disposal requirements,

95   end-users of passivated stainless steel such as NASA and the European Space Agency

96   (ESA) have been evaluating the performance of alternative acids, namely citric acid, as a

97   potential replacement for nitric acid for passivation [13].

98   Citric acid is a common metabolite of plants and animals, also present in the juice of citrus

99   fruits and pineapple. Its biological source and biodegradability make it a renewable and less

100   toxic alternative to nitric acid. The acid is predominantly used for soft drinks, confectionary,

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101 medicinal citrates, with smaller quantities used in dying and engraving [16]. On an industrial

102 scale it is predominately produced via fermentation of *Aspergillus* or *Candida.*

103 Despite the introduction of citric acid products such as CitriSurf® for stainless steel

104 passivation, to date there has lacked rigorous evaluation of chemical performance as a

105 passivation medium, and comparative assessment of its environmental impact compared

106 with nitric acid. The goal of this work is to compare nitric and citric acid production across a

107 range of environmental impact categories to understand whether biologically produced citric

108 acid can offer a greener, more environmentally friendly alternative to nitric acid passivation

109 whilst reaching comparable performance levels.

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111 2.0 Methods

112 This study is to contrasts the currently applied nitric acid passivation process with the most

113 suitable citric acid passivation process for selected types of pristine and welded stainless

114 steels.

115 The process evaluated in this LCA study is based on a laboratory-scale method for stainless

116 steel passivation. Primary data was collected based on processing methods employed by

117 ESR Technology Limited. Secondary sources include databases such as Ecoinvent 3.4 [17]

118 and published literature, which is referenced accordingly in section 2.2. LCA software

119 package Simapro 8 is used for the study.

120 The LCA evaluates a range of environmental impact categories as part of life cycle impact

121 assessment, based on the ILCD recommended midpoint impact assessment categories [18].

122 The full range of midpoint categories are reported: climate change, ozone depletion, human

123 toxicity (cancer and non-cancer), particulate matter, Ionizing radiation HH, Ionizing radiation

124 E (interim), photochemical ozone formation, acidification, terrestrial eutrophication,

125 freshwater eutrophication, marine eutrophication, freshwater ecotoxicity, land use, water

126 resource depletion, mineral, fossil and renewable resource depletion.

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2.1 Functional Unit and System Boundaries

129 Within LCA it is common for the environmental impacts to be calculated for the same given

130 service – the functional unit. The functional unit used for this study is *per 2000 cm2 of*

131 *stainless steel surface passivated*. This equates to the average surface area exposed during

132 one passivation process run in the ESR Technology laboratory. Surface area could be used

133 as a functional unit as it is assumed that each passivation process yielded a comparable

134 passivation performance. This equivalence was the basis of the ESR and ESA research into

135 the passivation processes - needing a functionally equivalent output on an area basis.

136 Cut-off rules (relating to environmental significance of certain materials and energy flows)

137 were not formally applied to the study; however, some inputs to the process were omitted for

138 both citric and nitric acid passivation. This includes some laboratory disposables used in the

139 cleaning of the stainless steel samples, such as disposable knitted polyester cloths and pH

140 testing paper. This is due to an inability to model these inputs to a reasonable level of

141 accuracy. Also omitted from this work are inputs relating to bagging and storage of samples,

142 as the conditions for doing this are assumed to be the same for each acid assessment. The

143 input of the stainless steel into the passivation process is outside the system boundary of

144 this work. This was done to ensure focus on the passivation process itself, as for nitric or

145 citric acid the input of stainless steel is assumed to be the same.

146 The system boundary is given in Figure 1. This includes all activities associated with the

147 cleaning, acid bath passivation, and subsequent washing and drying of samples. Impacts

148 are allocated 100% to the functional unit.

149 There are 3 stainless steels evaluated: AISI 410, PH17-7, and AISI 302. This was done in

150 order to take into account the different processing conditions required for different types of

151 stainless steel based on chromium content. AISI 410 is Martensitic with a lower alloy content

152 (~12.5% chromium, 0% nickel content). AISI 302 contains ~18% chromium, 9% nickel, and

153 PH17-7 contains ~17% chromium, 7% nickel.

154 The three passivation scenarios were evaluated: 50% nitric acid heated to 55°C and held at

155 temperature for 30 minutes (for AISI 302/PH 17-7 and AISI 410 stainless steels); 4% citric

156 acid heated to 60°C and held at temperature for 1 hour (AISI 302/PH 17-7 stainless steels);

157 and 10% citric acid heated to 80°C and held at temperature for 3 hours (AISI 410 stainless

158 steel only – accounting for lower alloying content).

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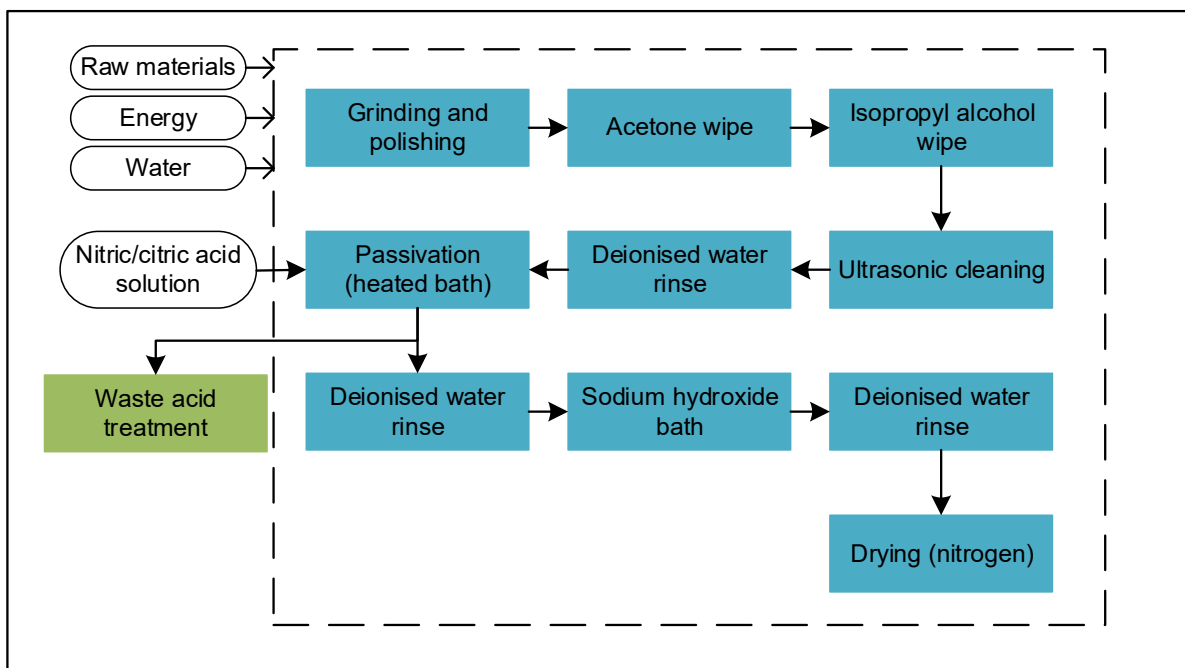
161 Figure 1. Process flow based flow for stainless steel passivation at laboratory scale (dotted line indicates process
162 steps, full line indicates system boundaries

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164 ## 2.2 Data collection and modelling

165 The LCI was modelled based on primary data from ESR. Material inputs were modelled

166 using Ecoinvent 3.4, and are shown in Table 1. An outline of the process is shown in figure

167   1. The abrasive paper used to polish the samples in the first process step was modelled

168   based on a 3M abrasive paper specification. The acetone wipes used to clean the samples

169   (3 samples per wipe) excluded the knitted polyester wipe used to apply the acetone. The

170   same omission was applied to the application of isopropyl alcohol with a polyester wipe.

171   The model for the Lenium® cleaning solution was based on its MSDS data sheet [19]. The

172   two major components of the solution n-propyl bromide and 2-propanol were modelled using

173   production data from Ecoinvent (Simpro inputs available in Supplementary Material).

174   For the passivation process direct electricity demand was modelled based on primary data

175   from ESR. The 3.5l acid bath containing solutions of 4%, 10% w/w citric acid and 50% w/w

176   nitric acid was modelled using data from Ecoinvent. Subsequent neutralisation with sodium

177   hydroxide, rinsing with deionised water and drying with gaseous nitrogen was also all

178   modelled using data from Ecoinvent. Heating of the sodium hydroxide solution to 70°C on a

179   laboratory hot plate was modelled using energy meter data at the University of Bath. The

180   bagging and storing of samples is not included in the scope of the study.

181   Electricity production is modelled using the Digest of United Kingdom Energy Statistics

182   (DUKES) [20]. This assumes a 2015 UK energy mix and assumes a mix broken down in the

183   following way: 22% coal, 30% natural gas, 21% nuclear, and remaining proportion from

184   renewables.

185   Within the LCA model, acid waste is treated differently depending on whether it is citric or

186   nitric acid. Spent nitric acid from the passivation bath (which is assumed to be emptied after

187   every six samples) is treated by waste solvent incineration. Spent citric acid, emptied from

188   the passivation bath at the same frequency as the nitric acid, is treated as effluent to waste

189   water treatment. Within the main LCIA, waste treatment is included as a sub-process within

190   the passivation step.

191 Waste management is also modelled separately in EcoSolvent [20] to evaluate each acid

192 under different waste management scenarios: incineration and waste water treatment.

193 Again, this assumes the passivation bath is emptied after each six sample batch.

194 The model assumes a large waste-solvent incineration plant, where the co-products of the

195 incineration plant are steam and electricity. Waste water treatment is calculated as a function

196 of the waste water composition. The model provides generic and site-specific data ranges

197 for mechanical-biological treatment, reverse osmosis and extraction. It is adapted to fit the

198 chemical properties of nitric and citric acid.

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205 Table 1. Inventory for 2000 cm2 passivation of stainless steel

Item	Process input	Comment
Grit paper	6 pieces	Based on 3M grit paper 12.5% silicon carbide, 87.5% paper backing
Acetone	30 ml	Primary data (ESR)
Isopropyl alcohol	30 ml	Primary data (ESR)
Lenium® solution	0.15 kg	Primary data (ESR) based on 85% n-propyl bromide and 10% 2 propanol
Ultrasonic cleaning bath	1.92 kWh	Primary data (ESR) based on 85% n-propyl bromide and 10% 2 propanol
Deionised water	5.2 kg	Primary data (ESR)
Passivation		
50% nitric acid		
Nitric acid	1.75kg	Primary data (ESR)
Bath heating	0.21 kWh	Primary data (ESR)
Fume hood operation	0.93 MJ	Calculated based on Caltech fume hood energy calculator: http://fumehoodcalculator.lbl.gov/
4% citric acid		
Citric acid	0.14kg	Primary data (ESR)
Bath heating	0.52 kWh	Primary data (ESR)
Fume hood operation	1.8 MJ	Calculated based on Caltech fume hood energy calculator: http://fumehoodcalculator.lbl.gov/
10% citric acid		
Citric acid	0.35kg	Primary data (ESR)

Bath heating	3.3 kWh	Primary data (ESR)
Fume hood operation	5.6 MJ	Calculated based on Caltech fume hood energy calculator: http://fumehoodcalculator.lbl.gov/
Sodium hydroxide solution	2l	Primary data (ESR)

2.3 Assumptions and Limitations

There are a number of assumptions and limitations associated with the LCA study. The process is based on laboratory scale stainless steel passivation, therefore may not be indicative of passivation at industrial scale. The production of steel is not included within the scope of the LCA to allow direct comparison between passivation acids (with the production of citric and nitric acid included in the scope of the study). Some laboratory consumables are omitted from the study, such as polyester wipes used for initial degreasing of the samples, as it has proved difficult to obtain inventory data to accurately represent these. These form only a very small part of the study and are their omission is therefore thought to have minimal impact on the results. As per standard LCA practice, the production of laboratory equipment is also not included within the scope of the assessment.

In the LCA study it is assumed that nitric and citric acid undergo different waste treatment options. Nitric acid is treated via waste solvent incineration, and citric acid via waste water treatment. There is uncertainty as to what would be the case at an industrial scale, and therefore waste treatment was also modelled separately in Ecosolvent.

3.0 Results and Discussion

3.1 Contribution analysis

The contribution of each processing step to the overall environmental impact of the whole passivation process was assessed using the ILCD recommended midpoint impact assessment categories. In this analysis everything is analysed as a percentage contribution

229   of the individual process. This indicates within each option which impact has the most

230   significant contribution.

231   The contribution results assess the following 3 scenarios for the passivation bath step:

- 50% nitric acid heated to 55°C and held at temperature for 30 minutes (AISI 302/PH 17-7 and AISI 410 stainless steels)
- 4% citric acid heated to 60°C and held at temperature for 1 hour (AISI 302/PH 17-7 stainless steel)
- 10% citric acid heated to 80°C and held at temperature for 3 hours (AISI 410 stainless steel)

239   Impact relating to acid usage and waste disposal is included as part of the passivation step.

240   Figure 2Figure 2 shows the contribution to total impact for the 4% citric acid scenario. Major

241   contributors to climate change impact (kg CO_2eq) are the ultrasonic cleaning step (55%) and

242   the passivation step (19%). Within both of these stages the main contribution to impact is

243   from process energy use – the operation of the cleaning bath or the passivation bath.

244   Further impact categories show a similar trend with ultrasonic cleaning and passivation step

245   dominating.
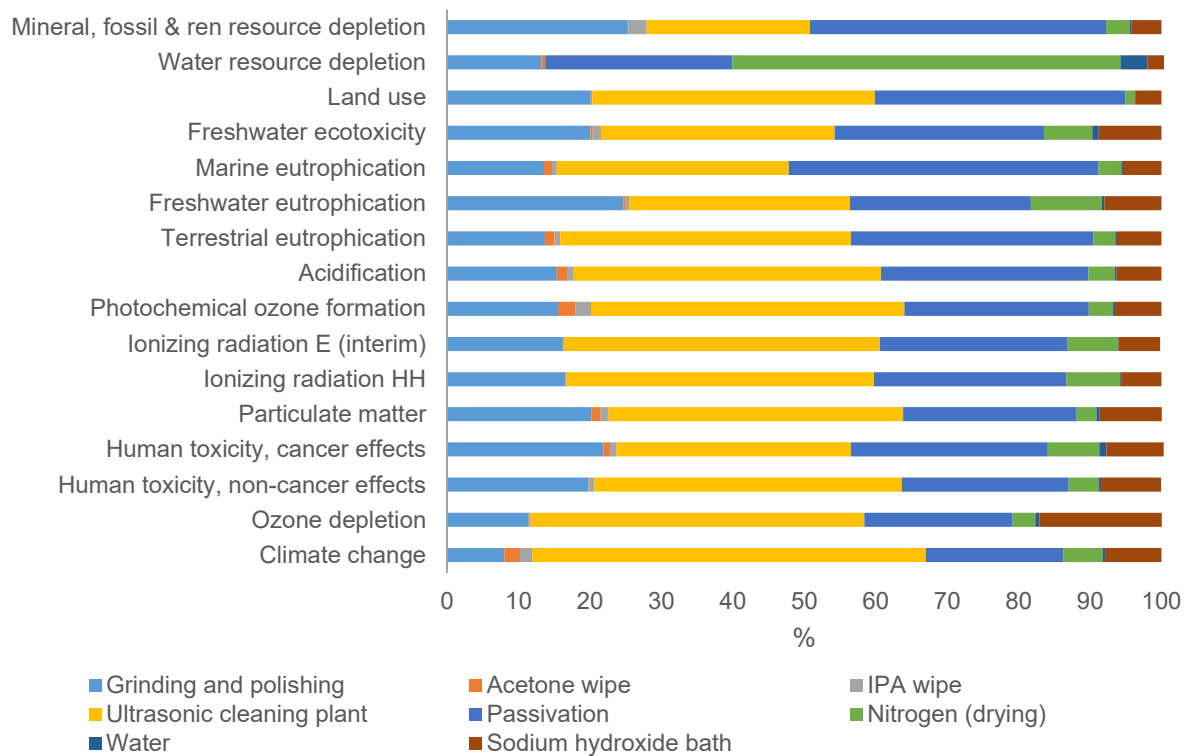
Figure 2 Contribution analysis for AISI 302/PH 17-7 4% citric acid

The passivation step is far more dominant for the 50% nitric acid scenario (Figure 3Figure 3). Here contribution to climate change impact is 83% of the total score. Passivation dominates other environmental impact categories. The dominance of the passivation step relates to the production of nitric acid. Nitric acid in Ecoinvent via the Ostwald process is dominated by ammonia production.
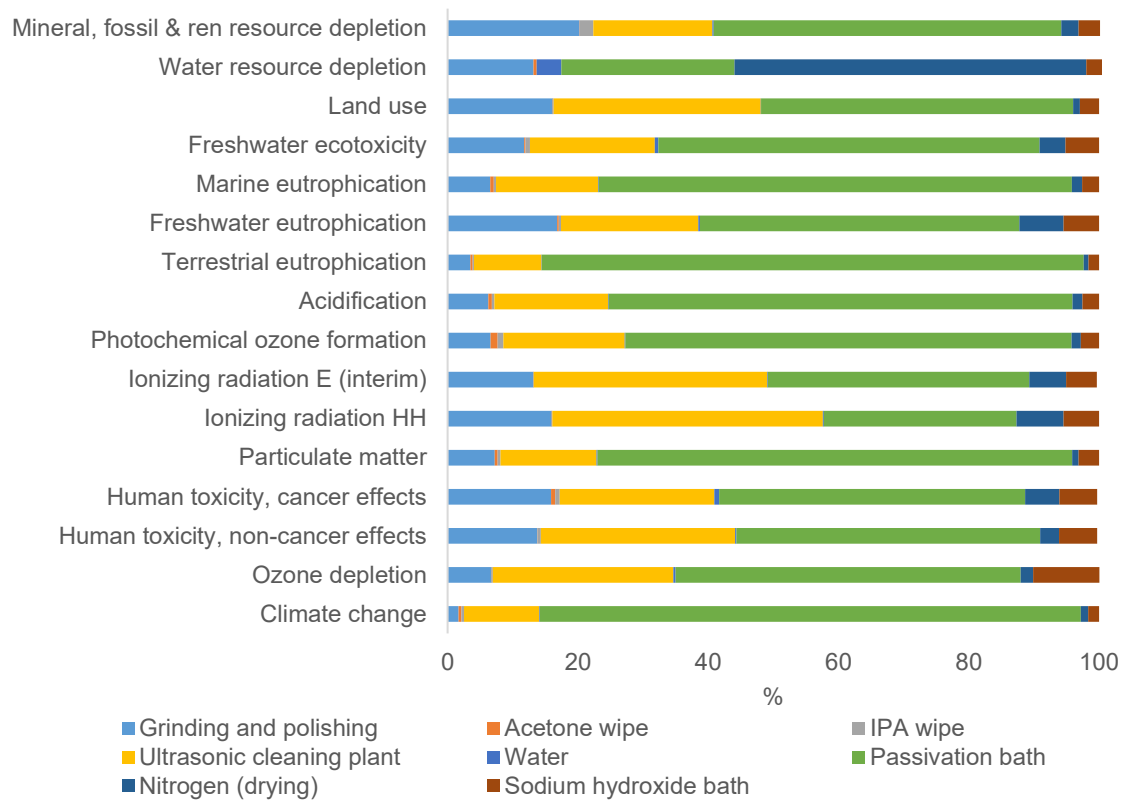
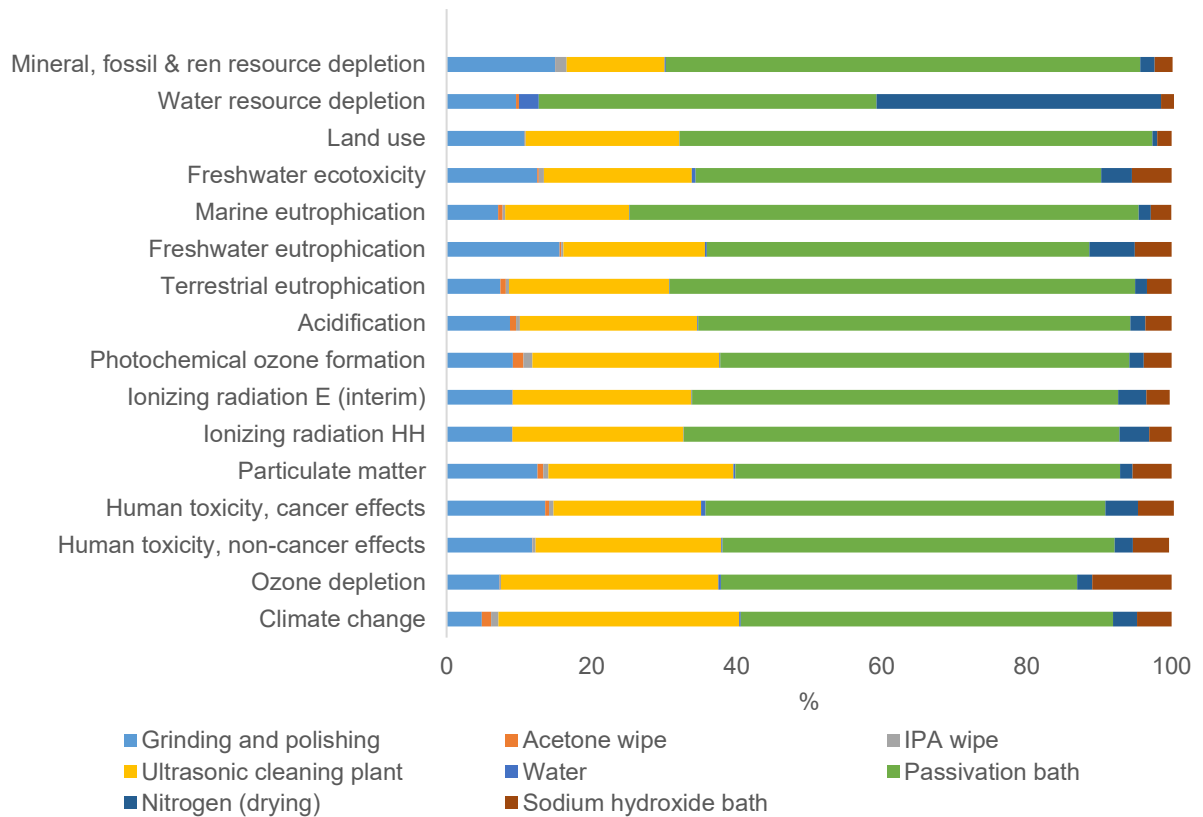Figure 3 Contribution analysis for AISI 302/PH 17-7 and AISI 410 50% nitric acid

The 10% citric acid scenario is used for the AISI 410 steel type only (figure 5). This has a far lower chromium and nickel alloy content (12.5% chromium, 0% nickel). Here the passivation step dominates impact for the majority of impact categories assessed. For climate change it contributes to 51% of overall impact. For freshwater ecotoxicity it contributes 56%, and for human toxicity (cancer and non-cancer) it contributes 55%. Sub-processes leading to the significant contribution of the passivation bath step to total impact are energy demand (bath operation) and production of citric acid. In this case citric acid is assumed to be produced via the fermentation of microorganism *Aspergillus niger*. Fermentation data is provided by a European citric acid producer, but the dataset aggregated by Ecoinvent to protect process confidentiality. Due to the contribution of the citric acid, further exploration undertaken in this area showed that although the process is widely known there is no published disaggregated data available on this. However, based on analysis of ecoinvent proxies (and previous

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267 evaluation by [22]) indicate that the impacts in citric acid production result predominantly

268 from the feedstock and any energy used in associated fermentation.

Figure 4 Contribution analysis for AISI 410 10% citric acid

3.2 Comparisons

273 All three passivation scenarios can be compared against each other (figure 5). All impacts

274 are compared with nitric acid as the reference, which is shown as 100% impact. Therefore,

275 effectively the two citric acid options are compared to nitric acid as the base case.

276 Comparing the 4% citric acid scenario used for AISI 302 and PH17-7 stainless steels against

277 the 50% nitric acid scenario used for all steels, the 4% scenario performs better across all

278 ILCD impact categories. For 8 out of the 16 ILCD impact categories for the 10% citric acid

279 scenario (AISI 410 stainless steel) has a higher environmental impact than the 50% nitric

280   acid scenario. This is due to the production of electricity required to heat the passivation bath

281   for three hours. Options to reduce this would include using a higher penetration renewable

282   technology for the heating, or heating in a more efficient way, if possible.

283   The comparisons made here show that despite the increased toxicity and environmental

284   impact from use of nitric acid as opposed to bio-based citric acid to passivate stainless steel,

285   where the process requires longer heating periods (10% citric acid scenario) and hence

286   higher process energy inputs this reduces some of the environmental gains made through

287   use of bio-based chemicals. The findings here highlight why multi-impact category

288   assessment methods like LCA are valuable for assessing green manufacturing alternatives.

289   Table 2 shows the characterised data in terms of absolute total values. The same data as in

290   Figure 5 is shown here, but not in terms of a percentage of the largest impact in each

291   category. Therefore, here one can compare the impact across the scenarios all the

292   scenarios in absolute terms for each scenario.
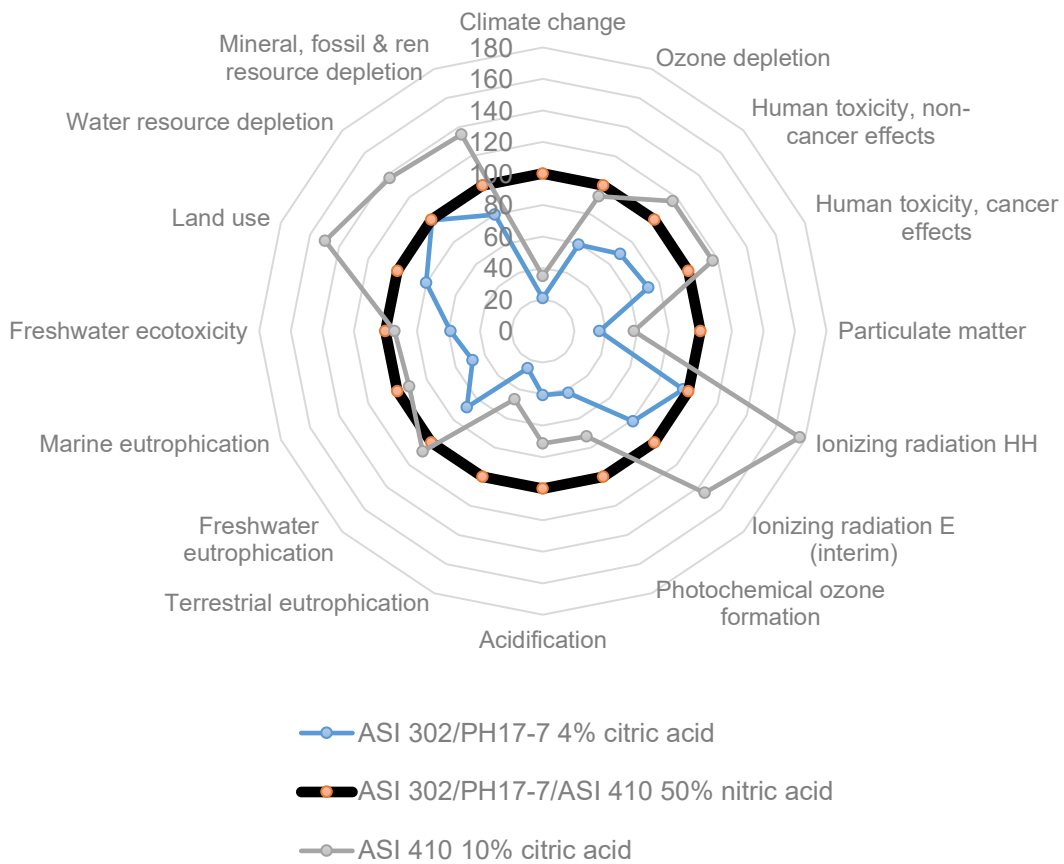
Figure 5. Comparison of each acid passivation scenario across all ILCD Recommended impact categories (nitric acid = 100%)

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305 Table 12. Breakdown of individual ILCD impact scores for each passivation scenario

Impact category	Unit	AISI 302/PH17-7 4% citric acid	AISI 302/PH17-7/AISI 410 50% nitric acid	AISI 410 10% citric acid
Climate change	kg CO2 eq	2.42E+00	1.15E+01	4.02E+00
Ozone depletion	kg CFC-11 eq	4.92E-07	8.29E-07	7.67E-07
Human toxicity, non-cancer effects	CTUh	8.39E-07	1.21E-06	1.41E-06
Human toxicity, cancer effects	CTUh	1.26E-07	1.74E-07	2.03E-07
Particulate matter	kg PM2.5 eq	1.89E-03	5.27E-03	3.04E-03
Ionizing radiation HH	kBq U235 eq	8.75E-01	9.07E-01	1.60E+00
Ionizing radiation E (interim)	CTUe	2.42E-06	2.99E-06	4.34E-06
Photochemical ozone formation	kg NMVOC eq	8.46E-03	1.99E-02	1.44E-02
Acidification	molc H+ eq	2.04E-02	5.02E-02	3.58E-02
Terrestrial eutrophication	molc N eq	3.40E-02	1.34E-01	6.27E-02
Freshwater eutrophication	kg P eq	1.17E-03	1.71E-03	1.85E-03
Marine eutrophication	kg N eq	3.73E-03	7.73E-03	7.10E-03
Freshwater ecotoxicity	CTUe	1.89E+01	3.22E+01	3.03E+01
Land use	kg C deficit	1.03E+01	1.28E+01	1.91E+01
Water resource depletion	m3 water eq	2.25E-02	2.26E-02	3.11E-02
Mineral, fossil & ren resource depletion	kg Sb eq	1.80E-04	2.25E-04	3.04E-04

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3.3 Acid waste treatment

308 Aside from potentially different processing conditions for citric (4%, 10% scenarios) and nitric

309 acid during the stainless steel passivation process, the methods for acid disposal also differ.

310 Nitric acid is highly corrosive and a strong oxidiser meaning that the 50% nitric acid solution

311 within the passivation bath will require special handling. It is likely that it would be disposed

312 of via a formal solvent disposal route as opposed to an industrial waste water treatment

313 system. Within the LCA model itself the nitric acid is assumed to be incinerated, whereas the

314 citric acid is treated via waste water treatment. For transparency, the disposal methods are

315 compared using Ecosolvent, which is a life cycle assessment tool developed by ETH Zurich

316 to quantify impacts relating to waste solvent treatment [20]. The tool models a hazardous

317 waste solvent incineration plant, and an industrial waste water treatment plant. Coproducts

318 from the incineration plant are steam and electricity, with environmental credits granted for

319 these.

320 Ecosolvent holds data for 26 solvents based on their elemental composition, heat of

321 vaporisation, and heating value. The model for these was adapted for nitric and citric acid

322 using their chemical property information. The incineration model calculates inventory data

323 for solvent combustion as a function of chemical composition. The model is based on data

324 for a Swiss incineration plant with a capacity of 35,000 tonnes per year. Results from each

325 waste scenario are reported in terms of their global warming potential

326 For the incineration scenario (figure 6), incineration energy recovery for all 3 scenarios is not

327 enough to counter direct emissions from the process. Per functional unit impact from solvent

328 production is far higher for nitric acid than for both citric acid scenarios. GWP totals for 10%,

329 4% citric acid and 50% nitric acid were 3.23, 2.37 and 7.52 kg CO_2eq respectively.

330 Impact from treatment at a waste water treatment plant (figure 7), despite not including any

331 energy recovery, is environmentally favourable for all acid passivation scenarios. Impact is

332 separated between solvent production, electricity and ancillaries in mechanical-biological

333 treatment and associated emissions (MBTP), sludge treatment, and waste water treatment

334 (WWTP). Impacts relating to reverse osmosis and extraction are zero. The relative GWP for

335 10%, 4% citric acid and 50% nitric acid scenarios is 1.79, 0.72, and 5.5 kg CO_2eq.

336 The results from modelling of waste treatment show that for both waste treatment options

337 nitric acid has the higher GWP potential compared with both 4% and 10% citric acid

338 scenarios. However, much of this additional impact comes from nitric acid production

339 (particularly for waste water treatment), rather than the waste disposal method selected.
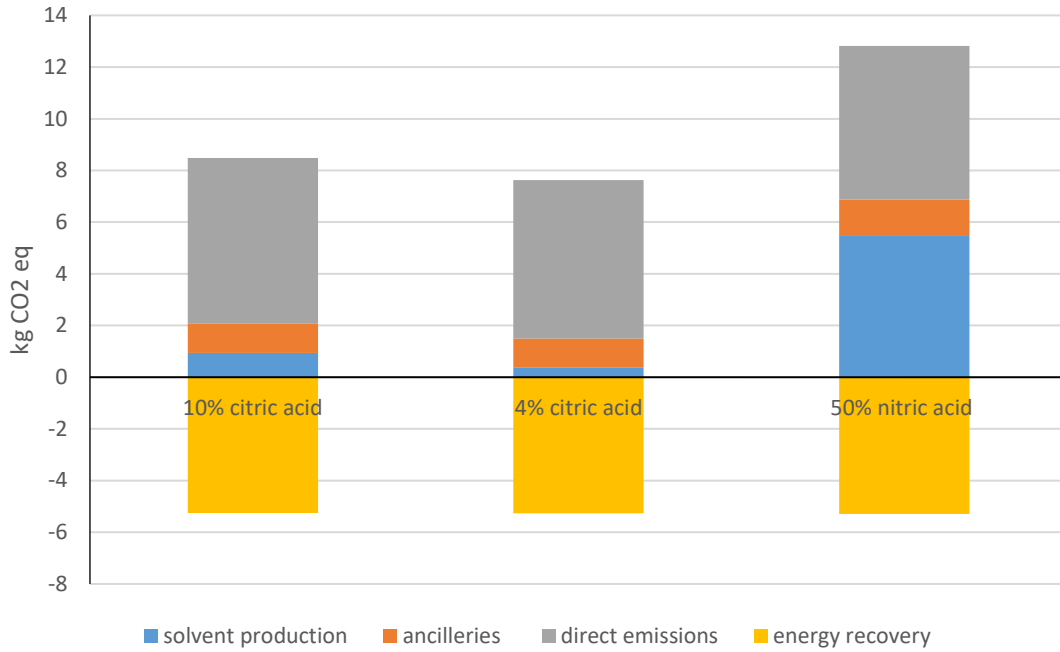
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341 Figure 6 Waste solvent treatment - Incineration. Global Warming Potential (GWP) per functional unit

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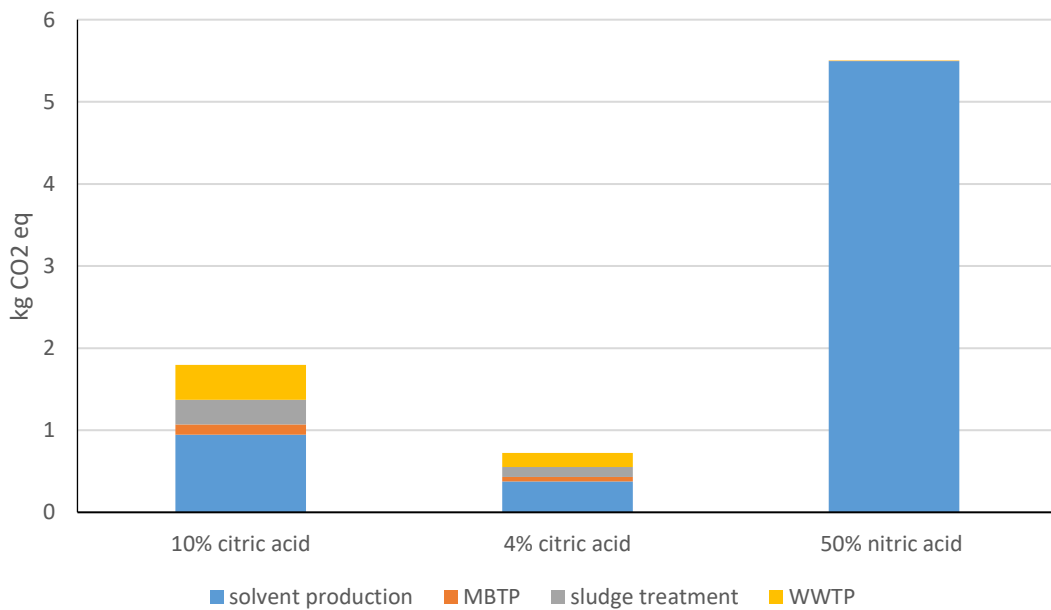
343 Figure 7 Waste solvent treatment. Waste water treatment plant. Global Warming Potential (GWP) per functional

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4.0 Conclusions

The use of green chemicals in manufacture and materials treatment processes, increases sustainability and helps to avoid difficult scale-up issues relating to chemical health and safety implications. Bio-based, renewable chemicals have the potential to be safer and have lower environmental impacts associated with both production and disposal stages of their life cycle than many conventional chemicals and solvents. However that is not always the case, and using Life cycle assessment (LCA) is a useful quantitative method for determining the comparative benefits or dis-benefits when selecting certain 'green' chemicals.

When treating stainless steel for corrosion resistance, there is increasing interest in passivating them using citric acid as opposed to nitric acid. Nitric acid is highly corrosive and toxic on inhalation, requiring heightened EHS criteria. This paper provides the first LCA of the potential benefits of citric acid over nitric acid as a passivation technique. This is based on the required conditions for passivation in order to generate the same corrosion resistance performance.

The LCA results show that the 4% citric acid scenario using AISI 302 and PH17-7 stainless steels, is environmentally preferable to 50% nitric acid across all ILCD recommended environmental impact categories. However, for the lower chromium and nickel content stainless steel AISI 410, the environmental benefits of moving to citric acid are less pronounced with only 50% of the ILCD impact categories assessed having a lower impact score than the nitric acid case. Impact associated with ionising radiation, resource depletion, and human toxicity were higher for the 10% citric acid scenario than for the nitric acid scenario. This is due to the increased time required within the heated passivation bath for the 10% citric acid scenario over the 4% citric acid, and 50% nitric acid scenarios.

This work demonstrates the importance of LCA as a method for evaluating processes which contain 'green' or bio-based chemicals. Evaluation across a number of different impact categories reveals a more nuanced picture of comparative environmental impact than that

374 given through use of singular assessment metrics. This is despite modelling approach

375 having been carried out at a laboratory scale and lead to potential misalignment with actual

376 processing at industrial scale. Process energy provision during passivation has been shown

377 to strongly influence the scale of environmental gains made by switching to a 'greener' acid

378 alternative.

Acknowledgements

Data availability

389 Primary data was provided by ESR Technology Limited. The raw data required to reproduce

390 these findings is available in the Supplementary Material. Processed data produced using

391 Simapro 8 and Ecosolvent is presented within the body of this paper.

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